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A NEW METHANOMETER WITHOUT ANY CALIBRATION

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ABSTRACT

In this paper, we explain how a new technique of heating a catalytic wire at a constant temperature, and a new method of measurement using two temperature levels, have allowed the development of a very performing multi-purpose methanometer, with no need for calibration during throughout the life of the sensor.

The main advantages are :

- improved reliability of the sensor since no compensating element is used,
- accurate measurement of the volumic ratio up to the lower explosive level, as required by the standards, even without of a compensating element,
- no zero or sensitivity drift, and hence no calibration required,
- low power consumption : heating the wire needs a 1 volt battery and takes only 0,08 ampere, giving long battery life,
- no uncertainty of the reading about the concentration (above or below stoichiometry).

INTRODUCTION

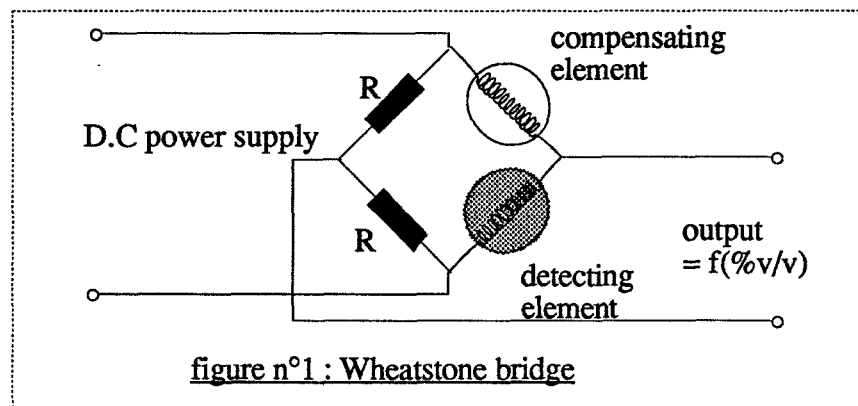
State of the art

The sensor most commonly used for detecting firedamp (methane) and measuring its concentration in mines is the catalytic sensor, which costs less than an infra-red detector.

The conventional catalytic sensor has two component parts - a detecting element and a compensating element - enclosed in a flameproof reaction chamber. The detector is a filament encased in a pellet of composite material, made up of alumina mixed with powdered metal (palladium or platinum) which acts as an oxidation catalyst.

The compensating element is identical with the detecting element, but its alumina pellet contains no catalyst. The two filaments are connected up in a Wheatstone bridge circuit (figure 1); a steady current flows through the filaments and raises the temperature of the pellets to about 600°C. In the presence of methane, the heat given off by oxidation of the methane in the detector pellet increases the filament temperature, causing a rise in its electrical resistance proportional to the temperature [1]. The bridge is then no longer balanced, a situation which the methanometer displays as a percentage of methane by volume.

Changes in the temperature and moisture content of the gaseous mixture influence the temperature of both filaments in the same way. Their resistances thus change by the same amount and the bridge remains in balance.



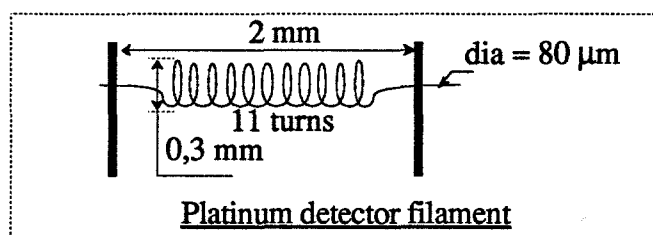
$$R_f = R_{f_0}(1 + KT) ; R_{f_0} = \rho \frac{L}{S} \quad [1]$$

A new sensor and a new electrical conditioning technique

The new catalytic sensor developed by INERIS is of simpler design in that it no longer has a compensating element, the result being lower power consumption and better reliability. To make up for the absence of a compensating element, a special technique is used for the electrical conditioning of the detector element, which cancels out the effects of changes in environmental parameters and improves the performance of the sensor and of the methanometer:

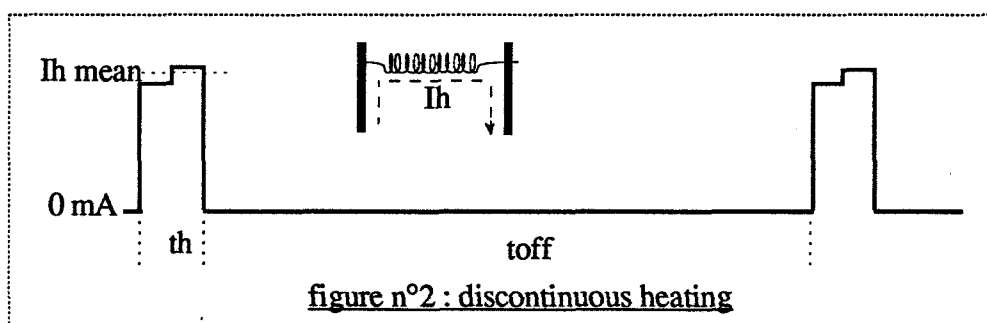
- there is less drift in the performance of the meter, obviating calibration and on-site maintenance,
- uncertainty is reduced,
- power consumption is much less.

The detector element is an extra-pure platinum wire.



CONDITIONING TECHNIQUE

The filament is used intermittently. It is heated for the minimum period of time needed to make a measurement, then switched off for as long as possible according to the desired response time for the particular application (this period of time can be programmed by the user) (figure 2). If t_h is the heating period, t_{off} the time during which the filament is switched off and $I_{h\text{ mean}}$ the mean heating current, then the mean current I_{mean} taken from the battery is equal to [2]:



$$I_{\text{mean}} = I_{h\text{ mean}} \times \frac{t_h}{t_h + t_{\text{off}}} \quad [2]$$

For an 80 μm filament: $I_{h \text{ mean}} = 1 \text{ A}$; $t_h = 0.4 \text{ s}$

if $t_{\text{off}} = 5 \text{ seconds}$:

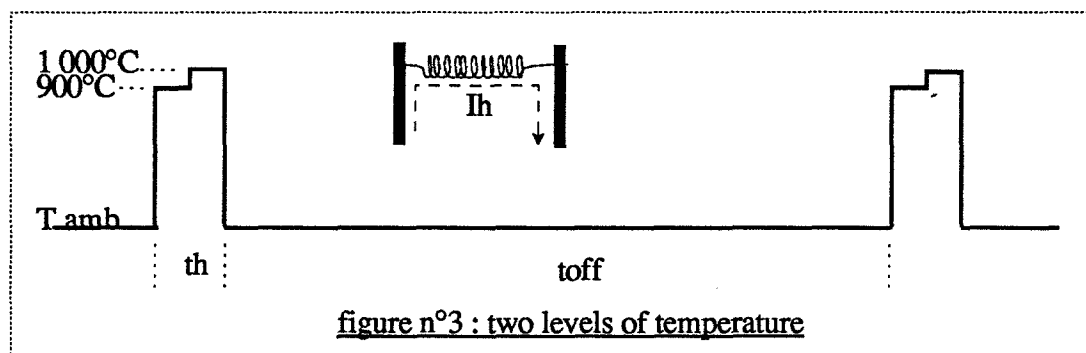
$$I_{\text{mean}} = 1 \times \frac{0,4}{5,4} \cong 0,08 \text{ A}$$

For a given response time, the power consumption is four times less than that of a continuously heated catalytic pellet and, having regard to the power taken by the compensating element, eight times less than that of the conventional sensor.

The heating of the filament incorporates two holding phases, at 900°C and 1000°C respectively (figure 3). The filament response is measured at these two temperatures, and the concentration then calculated by the methanometer using the formula:

$$\text{conc. in \% by vol.} = [\text{Resp}(1000^\circ\text{C}) - \text{Resp}(900^\circ\text{C})] \times K \quad [4]$$

The temperatures indicated are those at the centre of the filament.



Heating at constant resistance and temperature: filament response

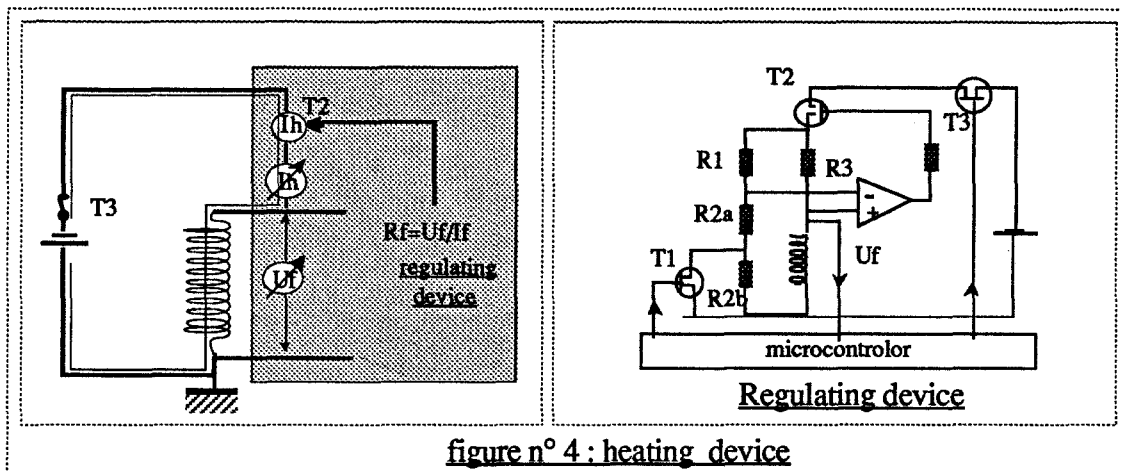
The filament operating temperature is maintained at 900°C and 1000°C by a control circuit which indirectly determines the temperature of the filament by measuring its hot resistance, and modifying the heating current to keep this resistance constant (figure 4).

When methane is present, the control circuit reduces I_h in order to compensate for the heat generated by the reaction.

The change in I_h which is proportional to the methane concentration constitutes the filament's response to this gas.

Note

It is important to control the filament temperature to ensure that it does not exceed 1000°C, for example when the methane oxidation reaction takes place; above this temperature, there is substantial evaporation of the platinum. Unless this precaution is taken, filament wear would be very rapid and its lifetime would depend on the quantities of methane it encounters. With constant temperature operation, filament wear depends only on the number of interrogations and can thus be modelled.



The response of the filament also results in a change in U_f which follows the change I_h . In fact $U_f = R_f \times I_h$ where R_f is constant by definition.

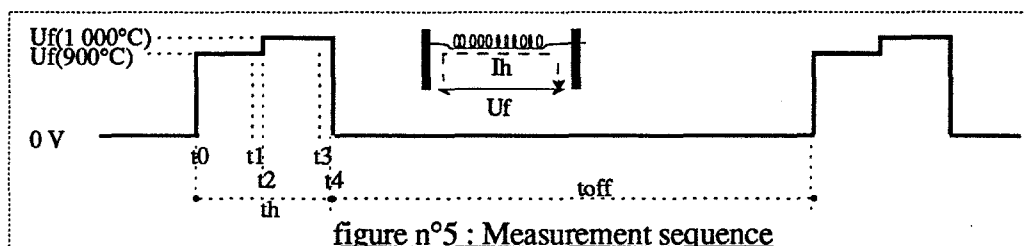
To calculate the response $U_f(T)$, the methanometer needs the value of $U_{f0}(T)$ in clean air $[U_{f0}(T)]$ in its memory.

The methanometer automatically measures and stores the value of $U_{f0}(T)$ when it is calibrated following the installation of a new filament. The air used should be free of any combustible gas but its temperature and relative humidity are unimportant.

$$\text{Resp}(1000^\circ\text{C}) = U_{f0}(1000^\circ\text{C}) - U_f(1000^\circ\text{C}) \quad [5]$$

$$\text{Resp}(900^\circ\text{C}) = U_{f0}(900^\circ\text{C}) - U_f(900^\circ\text{C}) \quad [6]$$

Measurement sequence (figure 5)



t_0 : filament heated to 900°C

t_1 : measurement of $U_f(900^\circ\text{C})$

t_2 : heating to 1000°C

t_3 : measurement of $U_f(1000^\circ\text{C})$

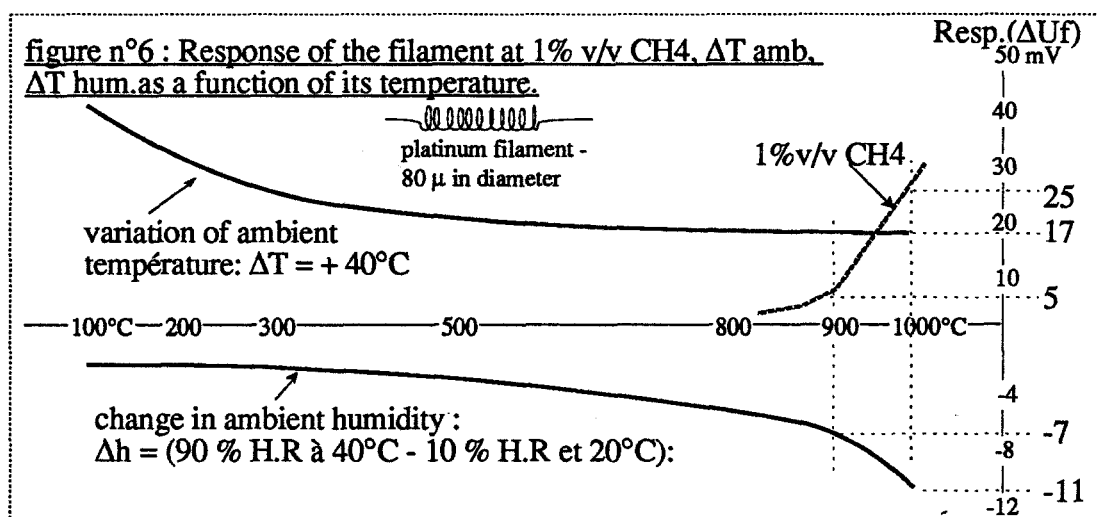
t_4 : heating turned off - calculation and display of concentration using the formulas [5][6][7]

$$C(\% \text{ by vol}) = [\text{Resp}(1000^\circ\text{C}) - \text{Resp}(900^\circ\text{C})] \times K \quad [7]$$

ADVANTAGES OF THE DIFFERENTIAL MEASUREMENT

Compensation for environmental factors

The differential measurement reduces the effects of environmental parameters. Figure 6 shows the response of the filament to these parameters for different heating temperatures.



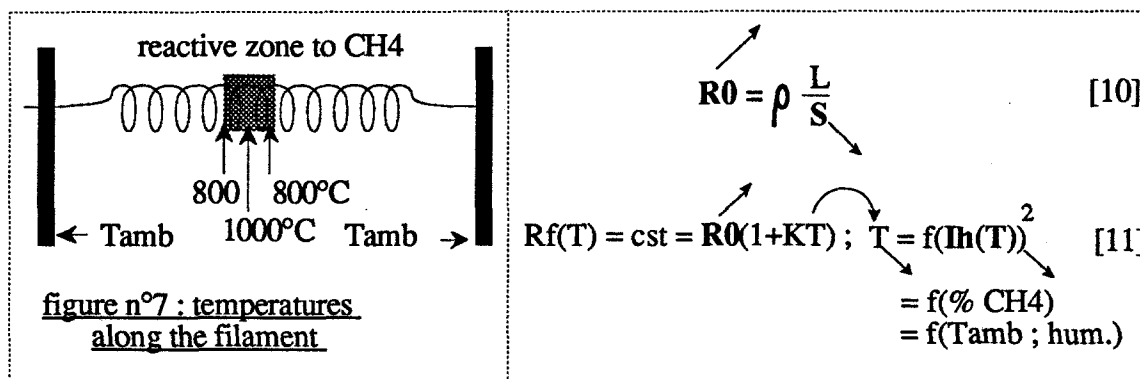
It can be seen that by subtracting the response at 1000°C from that at 900°C, the measurement for 1% by volume of CH₄ is 20 mV (25-5), for a substantial change in ambient temperature it is zero (17-7), and for a substantial change in relative humidity it is - 4 mV (- 11 + 7), or the equivalent of 0.20% by volume of CH₄; an error persists, but this is nevertheless within the tolerances of European standard 50 055 on methanometers covering the range 0-5% by volume. If all these parameters change at the same time, the response at T is the algebraic sum of the responses to each of the parameters taken separately.

The following table gives the responses and the measurement for the different parameters: CH₄, T_{amb}, relative humidity, and filament position, in the case where calibration was done using clean air in a room at 20°C with 50% RH.

parameters	CH ₄	temperature and humidity of the site				position
value	1% v/v	40°C air sec	0°C air sec	40°C 90% H.R	20°C 10% H.R	
response at 1000°C	25mV	9mV	-9mV	-7mV	+4mV	+2mV
response at 900°C	5mV	9mV	-9mV	-4mV	+2mV	+1mV
measure	20mV	0	0	-3mV	+2mV	+1mV
displayed concent.	1.00	0.00	0.00	- 0.15	0.10	+0,05

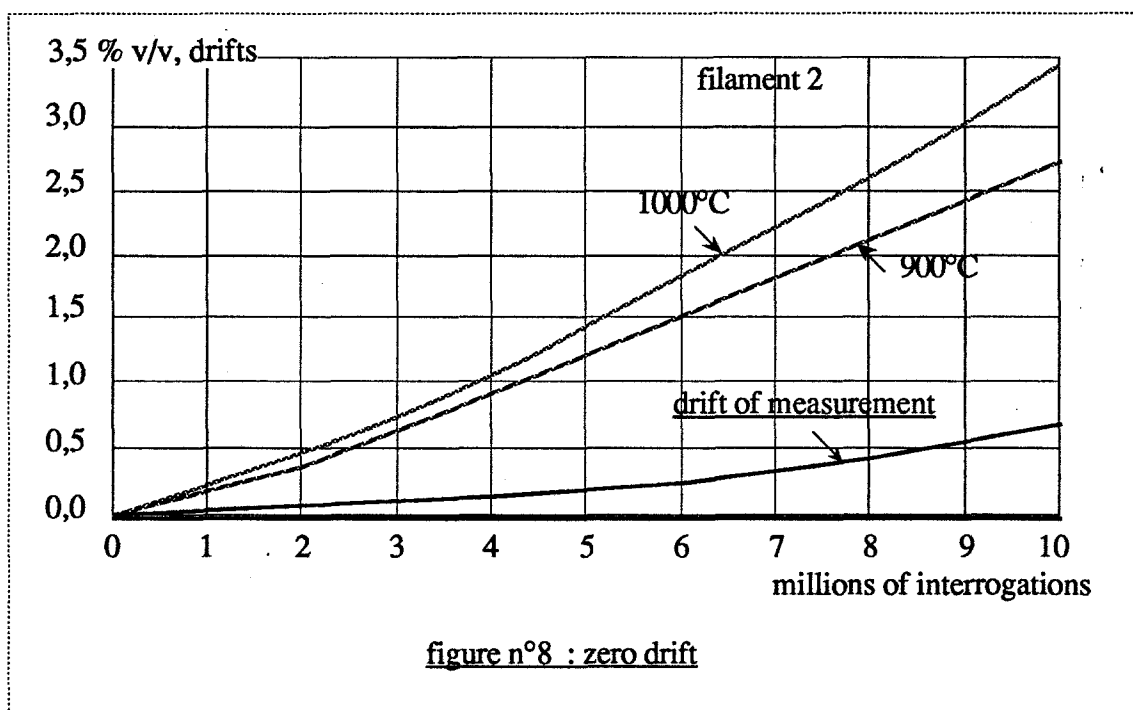
Reduced zero drift

Filament wear results in thinning of the most marked section in the hottest part, i.e., at the centre (figure 7).



R_0 thus increases with wear [10], with the result - owing to the principle of constant resistance heating - that there is a negative drift in the heating currents and in the response at 900°C and 1000°C [11].

Note: The measurements are thereby increased by an amount which rises with the number of interrogations. This quantity can be measured directly in clean air, hence it is known as the "zero drift". Figure 8 shows the drift in responses at 900°C and 1000°C, and the drift in the measurement which is the difference of the other two. The drift in the measurement is small and we have verified, by tests on a number of filaments, that it was reproducible. Thus the methanometer can automatically correct for this drift according to the number of interrogations accumulated since the new filament was fitted.



Reduced sensitivity drift

Owing to the principle of constant resistance heating, the temperature of the filament falls when R_0 increases, i.e., as the filament wears. The result is a negative drift in the responses to methane (figure 9). However the measurement, which is the difference between the two responses, falls less quickly than either of them (figure 10).

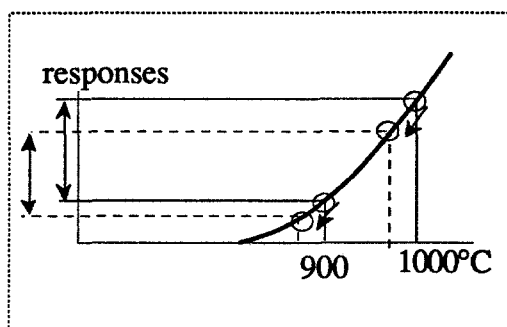


figure n°9 : drift of temperatures

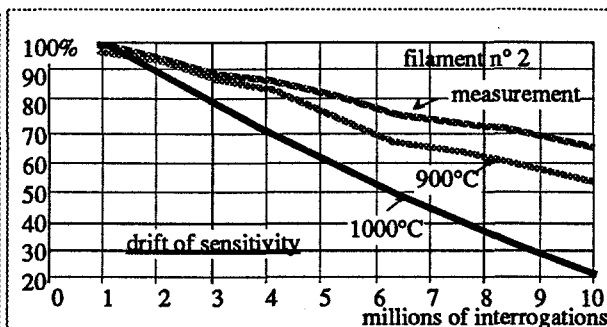


figure n°10 : drift of sensitivity

Just as for the zero drift, the reproducibility of this drift means that the methanometer can make an automatic correction according to the number of interrogations made since the filament was installed.

Less uncertainty

Methane is a better conductor of heat than air, and its conductivity increases with temperature (figure 11). This partly explains why, for a concentration greater than stoichiometric, the response at 900°C becomes greater than that at 1000°C, leading to a highly negative measurement (figure 12).

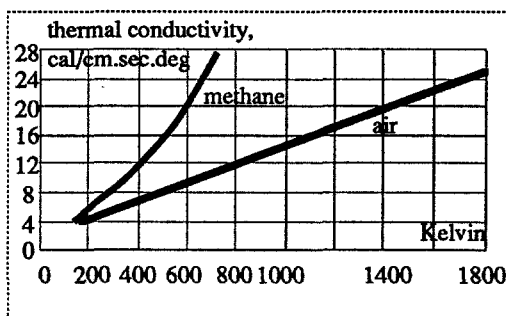


figure n°11 : thermal conductivity

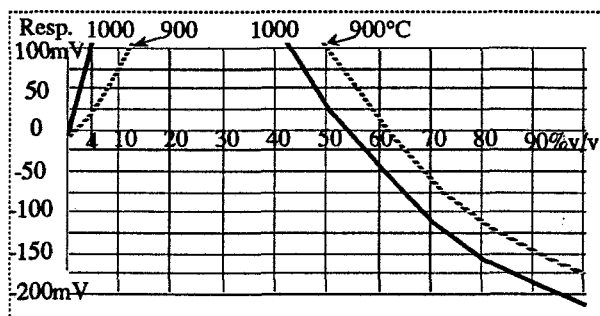
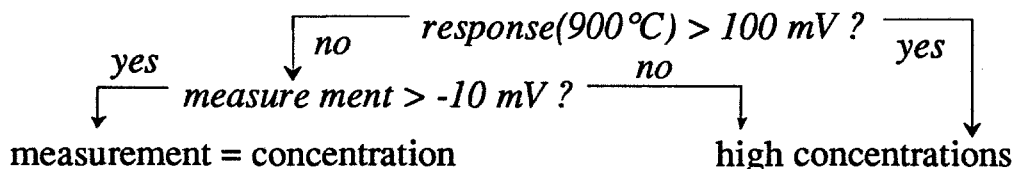


figure n°12 : responses to high concentrations

The methanometer makes use of this characteristic to recognise a high concentration. It applies the following algorithm:



RESULTS

A portable methanometer was built with an 80 μ filament used with these new techniques. Its characteristics are as follows:

- measurement scale: 0-4.0% by vol. - FSD 4 to 100% by vol.;
- filament life: > 8 million interrogations or 15 months for an interval of 5 seconds (30 months for an interval of 30 seconds);
- no maintenance: the methanometer requires no maintenance throughout the life of the sensor. The maximum measurement error would then be $\pm 0.25\%$ by vol. of CH_4 ;
- power consumption: 0.08 A for a 5-second interrogation interval; 0.04 A for an interval of 10 seconds;
- battery life: 40 hours for a interrogation interval of 5 s with a 4 Ah battery at 1.25 V.

PROSPECTS

Together with another French laboratory (LETT), INERIS is completing the development of a catalytic microfilament characterised by very low power consumption: the duration of heating is 0.08 s and the heating current is 0.15 A. According to [2], the current taken by the methanometer is only 2 mA for an interval of 5 s and 1 mA for an interval of 10 s. In these conditions the battery life is several months.